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PERMANGANATE	23968
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(31 AND PERMANGANATE).PGPB,USPT,USOC,EPAB,JPAB,DWPI,TDBD.	25
(L31 AND PERMANGANATE).PGPB,USPT,USOC,EPAB,JPAB,DWPI,TDBD.	25

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Search History

DATE: Thursday, December 08, 2005 [Printable Copy](#) [Create Case](#)

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DB=PGPB,USPT,USOC,EPAB,JPAB,DWPI,TDBD; PLUR=YES; OP=ADJ

<u>L34</u>	L31 and permanganate	25	<u>L34</u>
<u>L33</u>	L31 and textur\$4	8	<u>L33</u>
<u>L32</u>	l2 and L31	12	<u>L32</u>
<u>L31</u>	((circuit board) or (wiring board)) and L30	159	<u>L31</u>
<u>L30</u>	hydroxyl radical	12807	<u>L30</u>
<u>L29</u>	'mno.sub.4' and L25	0	<u>L29</u>
<u>L28</u>	'kmno.sub.4' and L25	0	<u>L28</u>
<u>L27</u>	permanganate and L25	0	<u>L27</u>
<u>L26</u>	board and L25	0	<u>L26</u>





<u>L25</u>	4740282	39	<u>L25</u>
<u>L24</u>	l22 and hydroxyl and permanganate	26	<u>L24</u>
<u>L23</u>	((circuit board) or (wiring board)) and L21 and 134/\$.ccls.	46	<u>L23</u>
<u>L22</u>	((circuit board) or (wiring board)) and L21	2711	<u>L22</u>
<u>L21</u>	free radical	100591	<u>L21</u>
<u>L20</u>	ep0913498	0	<u>L20</u>
<u>L19</u>	ep 0913498	0	<u>L19</u>
<u>L18</u>	ep 0510503	1	<u>L18</u>
<u>L17</u>	ep0510503	0	<u>L17</u>
<u>L16</u>	2001042682.an.	0	<u>L16</u>
<u>L15</u>	2001/042682	0	<u>L15</u>
<u>L14</u>	us2001042682	0	<u>L14</u>
<u>L13</u>	us2001042682.pn.	0	<u>L13</u>
<u>L12</u>	2001042682.pn.	3	<u>L12</u>
<u>L11</u>	5904155.pn.	2	<u>L11</u>
<u>L10</u>	4740282.pn.	2	<u>L10</u>
<u>L9</u>	4299863.pn.	2	<u>L9</u>
<u>L8</u>	wo 9606692	2	<u>L8</u>
<u>L7</u>	wo9606692	0	<u>L7</u>
<u>L6</u>	EP-1420620-A2.did.	2	<u>L6</u>
<i>DB=EPAB; PLUR=YES; OP=ADJ</i>			
<u>L5</u>	EP-1420620-A2.did.	1	<u>L5</u>
<u>L4</u>	EP-1420620-A2.did.	1	<u>L4</u>
<i>DB=PGPB,USPT,USOC,EPAB,JPAB,DWPI,TDBD; PLUR=YES; OP=ADJ</i>			
<u>L3</u>	L2 with (free radical)	14	<u>L3</u>
<u>L2</u>	smear\$4 or desmear\$4	50302	<u>L2</u>
<u>L1</u>	6790289.pn.	2	<u>L1</u>

END OF SEARCH HISTORY










Desmear and texturing method

Patent number: EP1420620
Publication date: 2004-05-19
Inventor: COBLEY ANDREW J (GB); GOOSEY MARTIN T (GB);
POOLE MARK A (GB)
Applicant: SHIPLEY CO L L C (US)
Classification:
- international: H05K3/00; C08J7/12
- european: H05K3/00K4B
Application number: EP20030256768 20031027
Priority number(s): GB20020025012 20021028

Also published as:

 US2004216761 (A1)
 JP2004282020 (A)
 EP1420620 (A3)
 CN1522105 (A)

Cited documents:

 WO9606692
 US4299863
 US4740282
 US5904155
 EP0510503
 WO0146298
 US2001042682 → ?
 EP0913498
 XP000117359
less <<

Report a data error here**Abstract of EP1420620**





A method for desmearing resin accretions from the surface of a substrate and texturing resins by generating a free radical which attacks and removes the resin accretions and textures the resin.

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
Desmear and texturing method

Patent number: EP1420620
Publication date: 2004-05-19
Inventor: COBLEY ANDREW J (GB); GOOSEY MARTIN T (GB);
POOLE MARK A (GB)
Applicant: SHIPLEY CO L L C (US)
Classification:
- international: H05K3/00; C08J7/12
- european: H05K3/00K4B
Application number: EP20030256768 20031027
Priority number(s): GB20020025012 20021028

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 US2004216761 (A1)
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Cited documents:

 WO9606692
 US4299863
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 US5904155
 EP0510503
 WO0146298
 US2001042682
 EP0913498
 XP000117359
less <<

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Abstract of EP1420620

A method for desmearing resin accretions from the surface of a substrate and texturing resins by generating a free radical which attacks and removes the resin accretions and textures the resin.

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define: smear

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Related phrases: [pap smear](#) [cervical smear](#) [smear test](#) [peripheral blood smear](#) [abnormal pap smear](#) [pat smear](#) [bronchoscopic smear](#) [also called pap smear](#) [smear champaign](#) [vaginal smear](#)

Definitions of **smear** on the Web:

- a specimen for microscopic examination of cells for detection of various conditions of the female genital tract (eg malignant and premalignant conditions), prepared by spreading the material across a slide.
www.uwo.ca/pathol/glossary.html
- Specimen material obtained from the surface of a mucous membrane for bacteriological or cytological examination. In gynecology, particularly for diagnosis of cervical cancer. Cells are scraped from the surface of the cervix and from the lining of the cervical canal and examined under the microscope (cervical smear or Pap test, named after the doctor Papanicolaou).
www.climodien.com/glossary/glossar.htm
- Undesirable artifact of CCDs that appears in the picture as a vertical streak above and below a very bright object in the scene. Smear is caused by parasitic light getting into the vertical transfer registers. It is greatly reduced by the microlens-type of CCD used in Hyper HAD and Power HAD sensors. Almost suppressed in FIT CCDs.
www.svsimaging.com/new_s.html
- a sample of cells spread across a glass slide to be examined through a microscope
www.american-depot.com/services/resources_gl_s.asp
- The spreading of ink, usually due to abrasion or rubbing of freshly (not yet set) printed ink to adjacent areas of the paper surface.
www.newpagecorp.com/mpd/home.nsf/Glossary
- A foothold in which the entire bottom of the front of the shoe is pasted on a smooth section of rock
www.rock-climbing.ws/rock-climbing-terminology/
- A term used to describe a picture condition in which objects appear to be extended horizontally beyond their normal boundaries in a blurred or "smeared" manner.
www.bcapa.com/about/glossary.php
- the technique of applying direct pressure to a smooth face thus creating an adhering friction for a hold
www.thinkwestkentucky.com/rockclimbing/glossary.html
- in jazz, a type of glissando or portamento in which the pitch of a note is shifted about a half step, often with a rather harsh tone
www.cgsmusic.net/Classical%20Guitar%20Sheet%20Music%20Dictionary/Classical%20Guitar%20Dictionary%20S.htm
- An unwanted side effect of vertical charge transfer in a CCD chip. It shows vertical bright stripes in places

of the image where there are very bright areas. In better cameras smear is minimized to almost undetectable levels.

www.retailspy.com/html/tech/glossary.htm

- to spread over a surface; to obliterate, obscure, blur, blend, wipe out, or defeat by or as if by smearing
www.chenzhonghua.com/Articles/cheng_taiji_glossary.htm
- a foothold made by friction alone. As much area of boot as possible is put in contact with the rock. Not a positive hold.
www.headcammer.co.uk/glossary.htm
- slanderous defamation
- stain by smearing or daubing with a dirty substance
- a thin tissue or blood sample spread on a glass slide and stained for cytologic examination and diagnosis under a microscope
- make a smudge on; soil by smudging
- daub: cover (a surface) by smearing (a substance) over it; "smear the wall with paint"; "daub the ceiling with plaster"
- smudge: a blemish made by dirt; "he had a smudge on his cheek"
- blot: an act that brings discredit to the person who does it; "he made a huge blot on his copybook"
- defame: charge falsely or with malicious intent; attack the good name and reputation of someone; "The journalists have defamed me!" "The article in the paper sullied my reputation"
wordnet.princeton.edu/perl/webwn

Find definitions of **smear** in: [English](#) [French](#) [German](#) [all languages](#)

define: smear

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L33: Entry 5 of 8

File: USPT

Mar 1, 2005

DOCUMENT-IDENTIFIER: US 6861097 B1

TITLE: Electroless plating processes

Abstract Text (1):

The invention includes processes for combined polymer surface treatment and metal deposition. Processes of the invention include forming an aqueous solution containing a metal activator, such as an oxidized species of silver, cobalt, ruthenium, cerium, iron, manganese, nickel, rhodium, or vanadium. The activator can be suitably oxidized to a higher oxidation state electrochemically. Exposing a part to be plated (such as an organic resin, e.g. a printed circuit board substrate) to the solution enables reactive hydroxyl species (e.g. hydroxyl radicals) to be generated and to texture the polymer surface. Such texturing facilitates good plated metal adhesion. As part of this contacting process sufficient time is allowed for both surface texturing to take place and for the oxidized metal activator to adsorb onto said part. The part is then contacted with a reducing agent capable of reducing the metal activator to a lower ionic form, or a lower oxidation state. That reduction can result in the formation of metallic catalytic material over the surface of the part. The reduced metal activator can then function to catalyze the electroless deposition of metal such as copper from solution by contacting the part with the plating solution.

Brief Summary Text (8):

In use, the metal activators are oxidized to a higher state (e.g. to Ag (II) or to Co (III)), preferably electrochemically. Without being bound by theory, it is believed the oxidized metal activator generates reactive hydroxyl species from water, such as hydroxyl radicals. These hydroxyl species are very reactive and attack polymer surfaces, particularly organic polymers, to give an ideal pitted morphology deemed desirable for subsequent metal adhesion and which is similar to that provided by chromic acid. In this process, following surface texturing the substrate is immersed in a reducing agent pre-dip solution and it can then be plated immediately by immersion in an electroless metal plating solution, e.g., copper bath without any further process steps. A further advantage of the invention is that the metal activator treatment solution (e.g. silver or cobalt solution) may be regenerated such as by electrochemical methods thus reducing problems encountered with waste treatment.

Brief Summary Text (10):

The present invention also is particularly useful in the manufacture of printed circuit boards. For example oxidizing agents such as potassium permanganate are used to remove resin smear and to provide a textured polymer surface prior to conditioning, catalyzation and electroless metal deposition. The use of transition oxidized metal species (e.g. Ag.sup.2+ or Co.sup.3+) in the production process removes several process steps and reduces chemical consumption.

Detailed Description Text (2):

According to the first aspect of the invention, a process is provided for metallizing a part, particularly a polymer substrate such as ABS, which has been etched by a reactive hydroxyl species (e.g. hydroxyl radicals) generated from water as a result of the presence a metal activator (e.g. Ag.sup.2+, Co.sup.3+) in the water, and applying a reducing agent capable of reducing the oxidized metal

activator species to a lower oxidation state (e.g. a zero oxidation state, or Ag.sup.2+ to Ag.sup.+, or Co.sup.3+ to Co.sup.2+). Any of a wide variety of reducing agents may be employed, e.g., a boron reagent such as a boron hydride or salts thereof e.g. sodium borohydride, and other boranes such as dimethylaminoborane; and other agents such as sodium dithionite, formaldehyde or a phosphite e.g., sodium hypophosphite, which is preferred. The oxidized metal activator species is typically generated electrochemically. After application of the reducing agent, electroless plating is employed, e.g., using electroless copper, nickel and the like to form a metal surface on the polymer substrate. In contrast to prior electroless processes, a Pd/tin, palladium, platinum or other electroless catalyst need not be employed to deposit effectively an electroless metal layer. In addition to ABS, other preferred polymers for metallization include e.g. polyamide, polycarbonate, ABS/polycarbonate blends, epoxy laminates particularly as used in printed circuit board manufacture, polyetherimides and liquid crystal polymers.

Detailed Description Text (4):

As yet a further aspect of this invention there is disclosed the use of electrochemically generated metal activator ions or oxidized species, such as silver.sup.2+ ions, Co.sup.3+, cerium (III) or (IV), iron (II) or (III), manganese (IV) or higher, nickel (II) (II) or (IV), ruthenium (V) (VI) (VII) (VIII), vanadium (IV) or (V), etc., in a combined surface treatment and metallization process where e.g. the silver ions generate hydroxyl radicals capable of texturing the polymer surface and which can also be reduced to silver metal on the surface so that the silver metal catalyses the subsequent electroless metal to be deposited thereon from a bath thereof, e.g. copper.

Detailed Description Text (5):

In order to achieve good quality metal deposits on polymers such as ABS, their surfaces are normally textured using aggressive solutions that provide a chemically and physically modified surface that is optimized for subsequent conditioning and electroless plating processes. Such materials that have been employed typically are strong oxidizing agents such as the alkali permanganates used with thermosets such as epoxides and chromic acid as used with thermoplastics such as Acrylonitrile Butadiene Styrene (ABS). The aim is to produce a reticulated textured surface that not only is amenable to conditioning with a subsequent surfactant but which also provides good keying and mechanical adhesion of the subsequently deposited electroless copper or other metal.

Detailed Description Text (9):

Using an inert electrode such as platinum, platinized titanium, platinum on niobium or tantalum, ruthenium or iridium dioxide on titanium, or carbon (glassy or vitreous) and a current density of 1 mA/cm.sup.2 to 10 A/cm.sup.2 with 500 mA/cm.sup.2 being preferred for ABS, the oxidized metal activator species (e.g. Ag.sup.2+ or Co.sup.3+) form rapidly and can readily attack polymers such as ABS giving a nicely textured surface virtually identical to that produced with chromic acid. Subsequent processing with a reducing agent and electroless metal plating solution e.g., copper plating gives electroless copper deposits with adhesion values equal to or better than those from substrates metallized following conventional chromic acid treatment. Oxidized cobalt species can be generated without a divided electrochemical cell, providing further cost reductions and easier processing.

Detailed Description Text (14):

As a preferred embodiment of this invention oxidized metal activator species, which may be e.g. electrochemically generated Ag.sup.2+, Co.sup.2+ or Co.sup.3+ ions or species are employed in a combined surface treatment and metallization process where the oxidized metal activator species ions generate reactive hydroxyl species (e.g. hydroxyl radicals) capable of texturizing the polymer surface and which can also be reduced to a lower oxidation state metal activator (e.g. silver metal or

cobalt metal) on the surface so that the reduced metal catalyzes the subsequent electroless metal to be deposited thereon from a bath thereof e.g., copper, nickel, etc.

Detailed Description Text (15):

Silver ions normally exist in solution as the single charged Ag.sup.+ ion, as is typically found for example in solutions of silver (I) nitrate, silver (I) tefrafluoroborate, silver (I) perchlorate and silver (I) fluoride. However, under certain conditions silver can be oxidized further to the doubly charged Ag.sup.2+ ion or species. This ion is very reactive and can be used to attack virtually all organic materials including polymers. The Ag.sup.2+ ion in solution is not stable and through a series of reactions converts back to Ag.sup.+ , typically over a period of a few days. However, the reversion of Ag.sup.2+ to Ag.sup.+ leads to the generation of hydroxyl radicals and it is this species that is so aggressive towards organic chemical bonds.

Detailed Description Text (27):

FIG. 2 diagrammatically illustrates a preferred additive process of the invention to plate a printed circuit board, including the through holes. In Step 1 of that process, a printed circuit board substrate 10 having through holes 12 is provided. That substrate 10 may be a laminate material formed from ABS, polyamide, polycarbonate, polyetherimides, epoxies, etc., and blends thereof. In Step 2, the surface of substrate 10 is exposed to an oxidized metal activator, e.g., oxidized silver, cobalt or the like wherein the oxidized species may have been suitably generated electrochemically, as described above with respect to FIG. 1. In that Step 2, the substrate 10 is then exposed to a reducing agent, e.g. a borane, preferably to leave a metal 14 (e.g. Ag if oxidized Ag used as the metal activator) on the substrate. In Step 3, a photoresist 16 then is applied to the planar surfaces and exposed and developed to provide desired bared substrate areas 18. The photoresist may be a dry film or applied as a liquid resist. In Step 4, the treated substrate 10 is immersed or other treated in an electroless plating solution to provide additive electroless metal layers 20, which typically will be electroless copper layer. In Step 5, photoresist 16 is stripped using suitable materials, e.g. a commercial resist stripper solution, which often will be an alkali solution. In Step 6, an etch may be employed if desired to remove any reduced metal activator 14 on the non-plated surfaces of substrate 10.

Detailed Description Text (28):

FIG. 3 diagrammatically illustrates a preferred pattern plate process of the invention to plate a printed circuit board, including through holes thereof. Steps 1 and 2 are the same as described above with respect to FIG. 2. Thus, in Step 1 of the process of FIG. 3, a printed circuit board substrate 40 having through holes 42 is provided. That substrate 40 again may be a laminate material formed from ABS, polyamide, polycarbonate, polyetherimides, epoxy resin, etc., and blends thereof. In Step 2, the surface of substrate 40 is exposed to an oxidized metal activator, e.g., oxidized silver, cobalt or the like wherein the oxidized species may have been suitably generated electrochemically, as described above with respect to FIG. 1. In that Step 2, the substrate 40 is then exposed to a reducing agent, e.g. a borane, preferably to leave a metal 44 (e.g. Ag if oxidized Ag used as the metal activator) on the substrate. In Step 3, the treated substrate 40 is immersed or other treated in an electroless plating solution to provide an electroless metal layer 46, which typically will be an electroless copper layer. In Step 4, a photoresist 48 then is applied to the planar substrate surfaces and exposed and developed to provide desired bared electrolessly plated substrate areas 50. The photoresist may be a dry film or applied as a liquid resist. In Step 5, the treated substrate 10 is electroplated, e.g. with copper or other metal to provide electrolytic metal layers 52. In Step 6, photoresist 48 is stripped using suitable materials, e.g. a commercial resist stripper solution, which may be an alkali solution. In Step 7, an etch may be employed to remove exposed electroless layer 46.

Detailed Description Text (35):

Metallization of FR4 Epoxy Circuit Board Substrate

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File: EPAB

May 19, 2004

PUB-NO: EP001420620A2

DOCUMENT-IDENTIFIER: EP 1420620 A2

TITLE: Desmear and texturing method

PUBN-DATE: May 19, 2004

INVENTOR-INFORMATION:

NAME	COUNTRY
COBLEY, ANDREW J	GB
GOOSEY, MARTIN T	GB
POOLE, MARK A	GB

ASSIGNEE-INFORMATION:

NAME	COUNTRY
SHIPLEY CO L L C	US

APPL-NO: EP03256768

APPL-DATE: October 27, 2003

PRIORITY-DATA: GB00225012A (October 28, 2002)

INT-CL (IPC): H05 K 3/00; C08 J 7/12

EUR-CL (EPC): H05K003/00

ABSTRACT:

CHG DATE=20040612 STATUS=O>A method for desmearing resin accretions from the surface of a substrate and texturing resins by generating a free radical which attacks and removes the resin accretions and textures the resin.

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L3: Entry 14 of 14

File: DWPI

Aug 18, 2004

DERWENT-ACC-NO: 2004-42252

DERWENT-WEEK: 200477

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TITLE: Desmearing substrate surface and texturing resin for use in manufacture of printed wiring boards for electrical applications, by generating free radical and contacting substrate surface with free radical

INVENTOR: COBLEY, A J; GOOSEY, M T ; POOLE, M A

PATENT-ASSIGNEE:

ASSIGNEE

CODE

SHIPLEY CO LLC

SHIL

ROHM & HAAS ELECTRONIC MATERIALS LLC

ROHM

PRIORITY-DATA: 2002GB-0025012 (October 28, 2002)

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PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
<input type="checkbox"/> CN 1522105 A	August 18, 2004		000	H05K003/06
<input type="checkbox"/> EP 1420620 A2	May 19, 2004	E	022	H05K003/00
<input type="checkbox"/> KR 2004038728 A	May 8, 2004		000	C08J007/16
<input type="checkbox"/> JP 2004282020 A	October 7, 2004		027	H05K003/42
<input type="checkbox"/> US 20040216761 A1	November 4, 2004		000	B08B003/12

DESIGNATED-STATES: AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LT LU
LV MC MK NL PT RO SE SI SK TR

APPLICATION-DATA:

PUB-NO	APPL-DATE	APPL-NO	DESCRIPTOR
CN 1522105A	October 28, 2003	2003CN-1125454	
EP 1420620A2	October 27, 2003	2003EP-0256768	
KR2004038728A	October 28, 2003	2003KR-0075357	
JP2004282020A	October 28, 2003	2003JP-0367474	
US20040216761A1	October 28, 2003	2003US-0695128	

INT-CL (IPC): [B08 B 3/12](#); [C08 J 7/12](#); [C08 J 7/16](#); [H05 K 1/00](#); [H05 K 3/00](#); [H05 K 3/06](#); [H05 K 3/42](#)

ABSTRACTED-PUB-NO: EP 1420620A

BASIC-ABSTRACT:

NOVELTY - Desmearing a substrate surface and texturing a resin includes generating free radical, and contacting substrate surface having resin accretions with the free radical to desmear the surface of the resin accretions and texture a resin.

USE - The method is used desmearing resin accretions from substrate surface and texturing a resin. It is useful in the manufacture of printed wiring boards for electrical applications. It is suitable for desmearing high glass transition temperature resin.

ADVANTAGE - The method eliminates the use of solvent swells and the hazards associated with solvent swells including waste disposal of environmentally hazardous chemicals. It also eliminates permanganate etch, reducing chemical consumption. The method is both worker and environmentally friendly.

CHOSEN-DRAWING: Dwg.0/5

TITLE-TERMS: SUBSTRATE SURFACE TEXTURE RESIN MANUFACTURE PRINT WIRE BOARD ELECTRIC
APPLY GENERATE FREE RADICAL CONTACT SUBSTRATE SURFACE FREE RADICAL

DERWENT-CLASS: A35 A85 L03 P43 V04

CPI-CODES: A11-C04; A12-E07A; L03-H04E9;

EPI-CODES: V04-R03G;

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1] 2004 ; P0000 Polymer Index [1.2] 2004 ; B9999 B5618 B5572 ;
N9999 N7227 N7023 ; K9927 ; B9999 B5378 B5276 ; B9999 B5492 B5403 B5276 ; Q9999
Q7454 Q7330 ; ND07

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C2004-158701

Non-CPI Secondary Accession Numbers: N2004-334940

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L34: Entry 7 of 25

File: PGPB

Nov 14, 2002

DOCUMENT-IDENTIFIER: US 20020169098 A1

TITLE: Cleaning composition

Summary of Invention Paragraph:

[0037] Both organic and inorganic substrates can be cleaned by the process of the invention. Representative examples of the substrates include metals; ceramics; glass; polycarbonate; polystyrene; acrylonitrile-butadiene-styrene copolymer; natural fibers (and fabrics derived therefrom) such as cotton, silk, fur, suede, leather, linen, and wool; synthetic fibers (and fabrics) such as polyester, rayon, acrylics, nylon, and blends thereof; fabrics comprising a blend of natural and synthetic fibers; and composites of the foregoing materials. The process is especially useful in the precision cleaning of electronic components (e.g., circuit boards), optical or magnetic media, and medical devices.

Detail Description Paragraph:

[0049] The atmospheric lifetime (t.sub.sample) of various sample compounds was calculated by the technique described in Y. Tang, Atmospheric Fate of Various Fluorocarbons, M. S. Thesis, Massachusetts Institute of Technology (1993). According to this technique, an ultraviolet (UV) gas cell was charged with a sample compound, a reference compound (either CH.sub.4 or CH.sub.3Cl), ozone, and water vapor. Hydroxyl radicals were then generated by photolytic decomposition of the ozone in the presence of the water vapor and an inert buffer gas, i.e., helium. As the sample compounds and reference compounds reacted with the hydroxyl radicals in the gas phase, their concentrations were measured by Fourier transform infrared spectroscopy (FTIR). The rate constant for reaction of the sample compound (k.sub.sample) with hydroxyl radical was measured relative to the rate constant for a reference compound (k.sub.ref), and the atmospheric lifetime was then calculated using the following formula (where .tau..sub.CH4 and k.sub.CH4 are known values of 12 years and 6.5.times.10.sup.-15 cm.sup.3/molecule-sec, respectively): 1 sample = CH4 (k sample k ref) (k ref k CH4)

Detail Description Paragraph:

[0056] The chemical stability of the alkoxy-substituted perfluorocompounds used in the processes and compositions of the invention was also evaluated to determine their suitability for use in cleaning and coating applications. In these tests, a compound was contacted with a chemical agent such as aqueous sodium acetate, aqueous KOH, concentrated sulfuric acid, or potassium permanganate in acetone to determine the stability of the compound to base, acid, or oxidant, as described below:

Detail Description Paragraph:

[0060] To assess oxidative stability, potassium permanganate (20 g, 0.126 mole) was dissolved in acetone, and C.sub.4F.sub.9OCH.sub.3 (500 g of 99.9% purity, 2.0 mole) was added to the resulting solution. The solution was refluxed for four hours, with no indication that the permanganate had been consumed (as evidenced by the absence of brown MnO.sub.2). The refluxed solution was then distilled into a 500 mL Barrett trap filled with water. The lower fluorochemical phase of the resulting mixture was separated from the upper phase, was washed with four 1.5 L aliquots of water, and was dried by passage through a column of silica gel to yield 471 g of resulting product. Gas chromatographic analysis of the product revealed no evidence of

degradation of the starting perfluorocompound, indicating that the compound was stable in the presence of the oxidant.

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File: USPT

Sep 14, 2004

DOCUMENT-IDENTIFIER: US 6790334 B2

TITLE: Combined adhesion promotion and direct metallization process

Abstract Text (1):

A combined adhesion promotion method of a metal to a non-conductive substrate and directly metallizing the non-conductive substrate with the metal. The method involves texturing a non-conductive substrate with a cobalt etch followed by applying a sulfide to the textured non-conductive substrate to provide an electrically conductive surface on the non-conductive substrate. After the surface of the non-conductive substrate has been made electrically conductive, the surface of the non-conductive substrate can be directly metallized. The method reduces the number of process steps for direct metallization of a non-conductive substrate. Thus, the method is more efficient in contrast to conventional methods of metallizing a non-conductive substrate.

Brief Summary Text (6):

EP 0 913,498 A1 provides an improvement over the electroless plating method of U.S. Pat. No. 4,734,299. EP 0 913,498 A1 discloses an electroless plating method where costly noble metals such as palladium need not be employed in catalytic metal colloids. Thus, the process is less costly. EP 0 913,498 A1 employs metal activators such as silver, cobalt, ruthenium, cerium, iron, manganese, nickel, rhodium and vanadium. The metal activators are applied to a non-conductive surface as salts such as sulfate salts in aqueous sulfuric acid solution, nitrate salts in nitric acid solution, fluoroborate salts in aqueous fluoroboric acid solution and the like. The metal activators provide a roughened surface on the non-conductive substrate without the need for harsh conditioning agents such as chromic acid and permanganate. In use, the metal activators are oxidized to a higher state (e.g. to Ag.sup.2+ or to Co.sup.3+) electrochemically. Workers in the art believe that the oxidized metal activator generates reactive hydroxyl species from water, such as hydroxyl radicals. The hydroxyl species are very reactive and attack the non-conductive surfaces, particularly organic polymers, to provide an ideal pitted or roughened morphology deemed desirable for subsequent metal adhesion. Following surface texturing, the non-conductive substrate is immersed in a reducing agent pre-dip solution. The substrate is then immediately plated by immersion into an electroless metal plating solution such as a copper bath without any further process steps. Examples of reducing agents employed in the process include formaldehyde, boron based reagents such as dimethylamineborane, boron hydride or salts thereof (e.g. sodium borohydride), sodium dithionite, or sodium hypophosphite.

Brief Summary Text (9):

Attempts have been made to avoid electroless plating processes by a direct metal plating process whereby a metal is deposited directly over a treated non-conductive surface. U.S. Pat. No. 5,007,990 discloses a method for direct electroplating the surface of a non-conductor and to articles manufactured by the process. The invention disclosed in the patent is based upon a combination of discoveries. One discovery was that chalcogenide films of metals that function as electroless deposition catalysts may be electroplated directly without requiring an intermediate electroless coating. Another discovery of the invention was that many of such chalcogenide films are insoluble and unaffected by treatment chemicals used

for plating of plastics and circuit board fabrication and therefore, the process of the invention was suitable for the formation of printed circuits using pattern plating processes.

Brief Summary Text (11):

Although U.S. Pat. No. 5,007,990 is an improvement in plating a non-conductive substrate by eliminating the electroless step from the process, the process preferably employs costly palladium metal over less costly metals such as copper, nickel, or cobalt. Additionally, when employing the process in the manufacture of printed circuit boards, board through-holes are desmeared by sulfuric acid, chromic acid or plasma etching or etchback of the holes with chromic acid prior to applying the process of the '990 patent. As discussed above, chromic acid steps are undesirable. Also use of sulfuric acid in its etching concentrations may present hazards to workers. Sulfuric acid may cause severe burns to workers and may cause corrosion of metal parts on printed circuit boards.

Brief Summary Text (15):

The present invention is directed to a combined process for improving the adhesion of a metal to a non-conductive substrate and direct metallization of the non-conductive substrate by texturing the non-conductive substrate with a cobalt etch and treating the textured non-conductive substrate with a sulfide to provide a conductive surface or layer. Advantageously, etching a non-conductive substrate with a cobalt etch texturizes the non-conductive substrate to provide a sufficiently roughened surface such that a metal deposited on the textured surface forms a bond of high integrity with the substrate. Further, the treatment of the cobalt etched non-conductive substrate with a sulfide provides a conductive cobalt sulfide species such that a metal can be directly plated on a now conductive surface of the non-conductive substrate.

Brief Summary Text (16):

Advantageously, the method of the present invention provides for an efficient method of texturing a non-conductive substrate and activating the non-conductive substrate to receive a metal deposit. The method of the present invention eliminates the steps of electroless plating as well as texturing the non-conductive substrate with an oxidizer such as hydrogen peroxide, chromic acid, permanganate and the like. The cobalt etch is sufficient to provide a textured surface on the non-conductive substrate without the use of an oxidizer. The method of the present invention also eliminates the use of undesirable reducing agents such as formaldehyde and boron compounds, and costly noble metal catalysts such as tin/palladium catalysts. Thus the method of the present invention not only provides a shorter and more efficient direct metallization process, but the process also eliminates the numerous problems associated with other metal plating methods.

Brief Summary Text (17):

Another advantage of the method of the present invention is that the method may be employed in both horizontal and vertical methods of manufacturing printed circuit and wiring boards. The method of the present invention is short, thus being highly suitable for horizontal circuit board manufacturing processes.

Brief Summary Text (18):

Horizontal methods are a highly desirable methods of preparing printed wiring boards because the process is more rapid than the vertical method, thus out-put is greater. Horizontal methods are more costly than vertical methods, because of the equipment employed, thus reducing the time of operation is highly desirable. The reduced number of method steps of the present invention to both texture and provide a conductive surface on the non-conductive substrate is highly desirable for horizontal methods.

Brief Summary Text (19):

A primary objective of the present invention is to provide for a method of

texturing and providing a conductive surface on a non-conductive substrate such that the substrate can be directly metallized.

Brief Summary Text (20):

Another objective of the present invention is to provide a method for texturing a non-conductive surface without the use of oxidizing agents.

Drawing Description Text (2):

FIG. 1 is a scanning electron micrograph (SEM) at 2000.times. of acrylonitrile-butadiene-styrene copolymer textured with an etching solution composed of cobalt sulfate in 1 M sulfuric acid; and

Drawing Description Text (3):

FIG. 2 is a scanning electron micrograph (SEM) at 2000.times. of acrylonitrile-butadiene-styrene copolymer textured with an etching solution composed of cobalt phosphate in 2.4 M phosphoric acid.

Detailed Description Text (2):

The present invention provides a combined adhesion and direct metallization method of a surface or layer of a non-conductive substrate by texturing a non-conductive substrate with a cobalt etch followed by treating the textured non-conductive substrate with a sulfide to provide a conductive surface or layer. Suprisingly, etching the non-conductive substrate with a cobalt salt solution without prior treatment of the non-conductive surface sufficiently roughens or texturizes the non-conductive surface to form a strong bond with a deposited metal. The roughened or textured non-conductive surface or layer is chemically and physically modified by the cobalt etch such that the surface is optimized for receiving a metal layer. The textured surface provides pores or micro-openings for both retaining cobalt ions that form a conductive species and a means for deposited metal to grasp onto to form a bond of high integrity. Application of the sulfide to the textured non-conductive substrate results in the formation of a conductive cobalt sulfide species that provides the non-conductive substrate with a conductive surface that can be directly metallized.

Detailed Description Text (4):

Preferably, but optionally, prior to texturing the non-conductive substrate with the cobalt etch, the non-conductive substrate is made hydrophilic with any suitable neutral pH conditioner or solvent swell. The pH of the conditioner or solvent swell may range from about 6.5 to less than about 8.0, preferably the pH of the conditioner or solvent swell ranges from about 7.0 to about 7.5. Conditioners or solvent swells are applied on the non-conductive substrate for about 1 minute to about 15 minutes, preferably from about 2 minutes to about 10 minutes. Optionally, the conditioned or solvent swell treated non-conductive substrate may be rinsed with water before applying the cobalt etch. The aqueous rinse step is performed for about 0.5 minutes to about 5 minutes, preferably from about 1 minute to about 3 minutes.

Detailed Description Text (8):

FIG. 1 shows a SEM at about 2000.times. of acrylonitrile-butadiene-styrene copolymer treated with a conditioner composed of a mixture of propylene carbonate and butyrolactone followed by etching with an aqueous solution of cobalt sulfate in 1 M sulfuric acid. The copolymer was first treated with the conditioner for about 5 minutes at about 40.degree. C., rinsed with water and then etched with the cobalt composition for about 15 minutes at about 35.degree. C. A current of about 0.2 amps (A) was passed through the etching solution during treatment. The SEM shows that the cobalt etching solution formed a highly porous or highly textured surface on the copolymer. Such high porosity or texturing provides for a surface where a directly electroplated metal can penetrate deep into the copolymer surface to form a uniform metal layer with a strong bond with the copolymer.

Detailed Description Text (10):

After application of the cobalt etch, the non-conductive substrate optionally may be rinsed with cold water. The aqueous rinse step is performed for about 0.5 minutes to 5 minutes, preferably from about 1 minute to about 3 minutes. Preferably, the etched non-conductive substrate is treated with the sulfide to form an electrically conductive cobalt sulfide species. The cobalt ions that are retained in the pores of the textured non-conductive substrate form the conductive sulfide species throughout the textured surface of the non-conductive substrate. The sulfide treatment step is from about 30 seconds to about 10 minutes, preferably from about 2 minutes to about 5 minutes. Any suitable sulfide that provides sulfide such that the cobalt sulfide conductive species is formed may be employed. Preferably, the sulfide is provided as an aqueous alkaline solution. The sulfide may be a monosulfide, disulfide, tetrasulfide or a polysulfide. Preferably, an alkali metal sulfide ($M_{\text{sub}2}S$, M =alkali metal) is used. Examples of suitable alkali metals include sodium, potassium, lithium and the like. Sodium sulfide ($Na_{\text{sub}2}S$) is the most preferred alkali metal sulfide. The sulfide solution contains from about 0.25 g/L to about 10 g/L of sulfide, preferably from about 0.5 g/L to about 5 g/L of sulfide.

Detailed Description Text (14):

After the sulfide treatment, a surface of the non-conductive substrate becomes conductive with the cobalt sulfide species. The now conductive and textured substrate may be directly metallized by any suitable direct electroplating procedure employed in the art. Optionally, the conductive substrate may be rinsed with water. The time period for rinsing with water is as disclosed above. Temperature ranges employed in the method steps of the present invention range from about 20.degree. C. to about 40.degree. C.

Detailed Description Text (17):

Substrates that are to be plated are employed as the cathode in electroplating cells. Any suitable anode may be employed in the electroplating cell apparatus, i.e., soluble or insoluble anodes. Current density may range from about 10 amps per ft.^{sup.2} to about 40 amps per ft.^{sup.2}, preferably from about 15 amps per ft.^{sup.2} to about 30 amps per ft.^{sup.2}. The electroplating solution is maintained at a temperature of from about 20.degree. C. to about 40.degree. C. Electroplating is continued until a desired thickness is formed on the substrate. For example, in the manufacture of printed circuit boards, a desired thickness may range from about 0.5 mils to about 2.0 mils, preferably from about 1.0 mils to about 1.5 mils. An electroplating time of from about 30 minutes to about 90 minutes is expected to obtain a deposit of the desired thickness within the above-mentioned ranges at the disclosed current density ranges.

Detailed Description Text (18):

Metal deposits formed by the process of the present invention are uniform in thickness and free of defects. Additionally, metal layers deposited on conductive surfaces of non-conductive substrates treated by the method of the present invention form a high integrity bond with the treated substrates. Bond strength is sufficient to withstand solder-shock testing as used in printed circuit board manufacture. Bond strengths between a deposited metal and a substrate treated using the cobalt etch may range from about 0.5 N/mm (Newtons/millimeter) to about 1.2 N/mm. More often the bond strength ranges from about 0.6 N/mm to about 0.8 N/mm.

Detailed Description Text (19):

Non-conductive substrates may be made from a variety of non-conductive materials, including resins such as thermoplastic, thermosetting and elastomeric polymers, and glass. The substrate may be a composite material, e.g., epoxy-glass, phenolic-paper, or polyester-glass; and composites used in printed circuit board manufacturing include polyimides for flexible circuitry or high-temperature applications; paper/phenolic that can be readily punched: NEMA grade FR-2; paper/epoxy that has improved mechanical properties than the paper/phenolic: NEMA

grade FR-3; glass/epoxy and woven glass fabric that have good mechanical properties: NEMA grade FR-4, FR-5; and random glass/polyester that is suitable for some applications: NEMA grade FR-6. Examples of thermosetting polymeric materials that are suitable include polyepoxides; phenolic resins; aminoplastics; unsaturated polyesters; polyimides; and polyamides. Preferred thermosetting polymeric materials include the epoxy resins; phenolic resins, e.g., copolymers of phenol, resorcinol and cresol; and polyamides. Non-conductive substrates can be molded from such polymeric materials additionally containing fillers and/or reinforcing agents, such as glass filled epoxy or phenolic base materials. Other additives that may be present in the polymer include natural fibers such as cotton, paper and cellulose; synthetic fibers; carbon black; powdered alumina; fine silica particles; wax and the like, used as fillers, pigments, reinforcing agents, mold release agents, and the like. Suitable thermoplastic polymeric materials include polyolefins, such high and low density polyethylene, polypropylene, polyfluoroethylene, ethylene-propylene copolymers and the like; polysulfones; polysulfides including polyalkylene sulfides and polyarylene sulfides; polystyrenes and acrylonitrile-butadiene-styrene (ABS) copolymers; polyimides; polyesterimides; polyetherimides; polycarbonates; polyphenylene oxide; polyurethanes; and polyamideimides. Preferred thermoplastic polymeric materials are polyolefins, e.g., polypropylene; polysulfones; polycarbonates; and ABS copolymers.

Detailed Description Text (20):

Advantageously, the method of the present invention provides for a method of both texturing and providing an electrically conductive surface on a non-conductive substrate that may be immediately electroplated. Prior to etching the non-conductive substrate with the cobalt etch, the non-conductive substrate need not be treated with corrosive or harsh compounds such as chromic acid. Surprisingly, the cobalt etch textures the non-conductive substrate such that a high integrity bond between the substrate and a metal deposited on the substrate is formed. In addition to eliminating harsh and undesirable treatment steps, the method of the present invention eliminates the need to employ costly tin/noble metal catalysts as well as an electroless plating step. Thus, the method of the present invention is both cost effective, and provides for a shorter method of achieving direct metallization of a surface of a non-conductive substrate. Because the method of the present invention has a shortened duration in contrast to conventional methods of electroplating non-conductive substrates, the method of the present invention may be effectively employed in both vertical and horizontal methods of preparing multi-layer circuit boards.

Detailed Description Text (35):

Accordingly, the combined adhesion promotion and direct metallization method of the present invention provided good texturing of an ABS polymer material as well as an efficient method for directly electroplating the ABS polymer material.

Detailed Description Text (39):

Accordingly, the combination cobalt etch and direct plating method of the present invention provided good texturing of a polymer material and an efficient direct electroplating method for metal on a polymer.

CLAIMS:

1. A method for direct metallization of a non-conductive substrate comprising: a) etching the non-conductive substrate with a cobalt etch solution to texture the non-conductive substrate such that the non-conductive substrate is made porous; then b) applying a sulfide to the porous non-conductive substrate to provide a conductive surface on the porous non-conductive substrate; and then c) metallizing the conductive and porous surface of the non-conductive substrate by direct electroplating.

11. A method for direct metallization of a non-conductive substrate consisting of:

a) conditioning a non-conductive substrate to make the non-conductive substrate hydrophilic; b) optionally rinsing the hydrophilic non-conductive substrate with an aqueous wash; c) texturing the hydrophilic non-conductive substrate with a cobalt etch to make a surface of the non-conductive substrate porous; d) optionally rinsing the porous surfaced non-conductive substrate with an aqueous wash; e) applying a sulfide to the porous surfaced non-conductive substrate to provide a conductive and porous surface on the non-conductive substrate; f) optionally rinsing the conductive and porous surfaced non-conductive substrate; and g) metallizing the conductive and porous surface of the non-conductive substrate by direct electroplating.

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File: USPT

Mar 1, 2005

DOCUMENT-IDENTIFIER: US 6861097 B1

TITLE: Electroless plating processes

Abstract Text (1):

The invention includes processes for combined polymer surface treatment and metal deposition. Processes of the invention include forming an aqueous solution containing a metal activator, such as an oxidized species of silver, cobalt, ruthenium, cerium, iron, manganese, nickel, rhodium, or vanadium. The activator can be suitably oxidized to a higher oxidation state electrochemically. Exposing a part to be plated (such as an organic resin, e.g. a printed circuit board substrate) to the solution enables reactive hydroxyl species (e.g. hydroxyl radicals) to be generated and to texture the polymer surface. Such texturing facilitates good plated metal adhesion. As part of this contacting process sufficient time is allowed for both surface texturing to take place and for the oxidized metal activator to adsorb onto said part. The part is then contacted with a reducing agent capable of reducing the metal activator to a lower ionic form, or a lower oxidation state. That reduction can result in the formation of metallic catalytic material over the surface of the part. The reduced metal activator can then function to catalyze the electroless deposition of metal such as copper from solution by contacting the part with the plating solution.

Brief Summary Text (8):

In use, the metal activators are oxidized to a higher state (e.g. to Ag (II) or to Co (III)), preferably electrochemically. Without being bound by theory, it is believed the oxidized metal activator generates reactive hydroxyl species from water, such as hydroxyl radicals. These hydroxyl species are very reactive and attack polymer surfaces, particularly organic polymers, to give an ideal pitted morphology deemed desirable for subsequent metal adhesion and which is similar to that provided by chromic acid. In this process, following surface texturing the substrate is immersed in a reducing agent pre-dip solution and it can then be plated immediately by immersion in an electroless metal plating solution, e.g., copper bath without any further process steps. A further advantage of the invention is that the metal activator treatment solution (e.g. silver or cobalt solution) may be regenerated such as by electrochemical methods thus reducing problems encountered with waste treatment.

Brief Summary Text (10):

The present invention also is particularly useful in the manufacture of printed circuit boards. For example oxidizing agents such as potassium permanganate are used to remove resin smear and to provide a textured polymer surface prior to conditioning, catalyzation and electroless metal deposition. The use of transition oxidized metal species (e.g. Ag.sup.2+ or Co.sup.3+) in the production process removes several process steps and reduces chemical consumption.

Detailed Description Text (2):

According to the first aspect of the invention, a process is provided for metallizing a part, particularly a polymer substrate such as ABS, which has been etched by a reactive hydroxyl species (e.g. hydroxyl radicals) generated from water as a result of the presence a metal activator (e.g. Ag.sup.2+, Co.sup.3+) in the water, and applying a reducing agent capable of reducing the oxidized metal

activator species to a lower oxidation state (e.g. a zero oxidation state, or Ag.sup.2+ to Ag.sup.+, or Co.sup.3+ to Co.sup.2+). Any of a wide variety of reducing agents may be employed, e.g., a boron reagent such as a boron hydride or salts thereof e.g. sodium borohydride, and other boranes such as dimethylaminoborane; and other agents such as sodium dithionite, formaldehyde or a phosphite e.g., sodium hypophosphite, which is preferred. The oxidized metal activator species is typically generated electrochemically. After application of the reducing agent, electroless plating is employed, e.g., using electroless copper, nickel and the like to form a metal surface on the polymer substrate. In contrast to prior electroless processes, a Pd/tin, palladium, platinum or other electroless catalyst need not be employed to deposit effectively an electroless metal layer. In addition to ABS, other preferred polymers for metallization include e.g. polyamide, polycarbonate, ABS/polycarbonate blends, epoxy laminates particularly as used in printed circuit board manufacture, polyetherimides and liquid crystal polymers.

Detailed Description Text (4):

As yet a further aspect of this invention there is disclosed the use of electrochemically generated metal activator ions or oxidized species, such as silver.sup.2+ ions, Co.sup.3+, cerium (III) or (IV), iron (II) or (III), manganese (IV) or higher, nickel (II) (II) or (IV), ruthenium (V) (VI) (VII) (VIII), vanadium (IV) or (V), etc., in a combined surface treatment and metallization process where e.g. the silver ions generate hydroxyl radicals capable of texturing the polymer surface and which can also be reduced to silver metal on the surface so that the silver metal catalyses the subsequent electroless metal to be deposited thereon from a bath thereof, e.g. copper.

Detailed Description Text (5):

In order to achieve good quality metal deposits on polymers such as ABS, their surfaces are normally textured using aggressive solutions that provide a chemically and physically modified surface that is optimized for subsequent conditioning and electroless plating processes. Such materials that have been employed typically are strong oxidizing agents such as the alkali permanganates used with thermosets such as epoxides and chromic acid as used with thermoplastics such as Acrylonitrile Butadiene Styrene (ABS). The aim is to produce a reticulated textured surface that not only is amenable to conditioning with a subsequent surfactant but which also provides good keying and mechanical adhesion of the subsequently deposited electroless copper or other metal.

Detailed Description Text (14):

As a preferred embodiment of this invention oxidized metal activator species, which may be e.g. electrochemically generated Ag.sup.2+, Co.sup.2+ or Co.sup.3+ ions or species are employed in a combined surface treatment and metallization process where the oxidized metal activator species ions generate reactive hydroxyl species (e.g. hydroxyl radicals) capable of texturizing the polymer surface and which can also be reduced to a lower oxidation state metal activator (e.g. silver metal or cobalt metal) on the surface so that the reduced metal catalyzes the subsequent electroless metal to be deposited thereon from a bath thereof e.g., copper, nickel, etc.

Detailed Description Text (15):

Silver ions normally exist in solution as the single charged Ag.sup.+ ion, as is typically found for example in solutions of silver (I) nitrate, silver (I) tefrafluoroborate, silver (I) perchlorate and silver (I) fluoride. However, under certain conditions silver can be oxidized further to the doubly charged Ag.sup.2+ ion or species. This ion is very reactive and can be used to attack virtually all organic materials including polymers. The Ag.sup.2+ ion in solution is not stable and through a series of reactions converts back to Ag.sup.+, typically over a period of a few days. However, the reversion of Ag.sup.2+ to Ag.sup.+ leads to the generation of hydroxyl radicals and it is this species that is so aggressive

towards organic chemical bonds.

Detailed Description Text (27):

FIG. 2 diagrammatically illustrates a preferred additive process of the invention to plate a printed circuit board, including the through holes. In Step 1 of that process, a printed circuit board substrate 10 having through holes 12 is provided. That substrate 10 may be a laminate material formed from ABS, polyamide, polycarbonate, polyetherimides, epoxies, etc., and blends thereof. In Step 2, the surface of substrate 10 is exposed to an oxidized metal activator, e.g., oxidized silver, cobalt or the like wherein the oxidized species may have been suitably generated electrochemically, as described above with respect to FIG. 1. In that Step 2, the substrate 10 is then exposed to a reducing agent, e.g. a borane, preferably to leave a metal 14 (e.g. Ag if oxidized Ag used as the metal activator) on the substrate. In Step 3, a photoresist 16 then is applied to the planar surfaces and exposed and developed to provide desired bared substrate areas 18. The photoresist may be a dry film or applied as a liquid resist. In Step 4, the treated substrate 10 is immersed or other treated in an electroless plating solution to provide additive electroless metal layers 20, which typically will be electroless copper layer. In Step 5, photoresist 16 is stripped using suitable materials, e.g. a commercial resist stripper solution, which often will be an alkali solution. In Step 6, an etch may be employed if desired to remove any reduced metal activator 14 on the non-plated surfaces of substrate 10.

Detailed Description Text (28):

FIG. 3 diagrammatically illustrates a preferred pattern plate process of the invention to plate a printed circuit board, including through holes thereof. Steps 1 and 2 are the same as described above with respect to FIG. 2. Thus, in Step 1 of the process of FIG. 3, a printed circuit board substrate 40 having through holes 42 is provided. That substrate 40 again may be a laminate material formed from ABS, polyamide, polycarbonate, polyetherimides, epoxy resin, etc., and blends thereof. In Step 2, the surface of substrate 40 is exposed to an oxidized metal activator, e.g., oxidized silver, cobalt or the like wherein the oxidized species may have been suitably generated electrochemically, as described above with respect to FIG. 1. In that Step 2, the substrate 40 is then exposed to a reducing agent, e.g. a borane, preferably to leave a metal 44 (e.g. Ag if oxidized Ag used as the metal activator) on the substrate. In Step 3, the treated substrate 40 is immersed or other treated in an electroless plating solution to provide an electroless metal layer 46, which typically will be an electroless copper layer. In Step 4, a photoresist 48 then is applied to the planar substrate surfaces and exposed and developed to provide desired bared electrolessly plated substrate areas 50. The photoresist may be a dry film or applied as a liquid resist. In Step 5, the treated substrate 10 is electroplated, e.g. with copper or other metal to provide electrolytic metal layers 52. In Step 6, photoresist 48 is stripped using suitable materials, e.g. a commercial resist stripper solution, which may be an alkali solution. In Step 7, an etch may be employed to remove exposed electroless layer 46.

Detailed Description Text (35):

Metallization of FR4 Epoxy Circuit Board Substrate

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